

MECHANISTIC STUDIES OF THE CO-OXIDATION REACTION ON
CATALYSTS FOR USE IN LONG-LIFE CO₂ LASERS¹

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SUMMARY

The catalytic recombination of carbon monoxide and oxygen has been studied under conditions expected to be present in a sealed E-beam CO₂ laser system. These conditions are typically a gas inlet temperature of 60°C, a substoichiometric CO/O₂ ratio of ca. 2.5/1 with an oxygen feed rate of ca. 5 micromoles/s, a carrier gas comprising He, N₂ and CO₂ in the ratio of 3:2:1, near atmospheric pressure and a gas velocity of 4 m/s. Heterogeneous catalysts, based on precious metal supported on tin oxide, have been coated onto ceramic monoliths and tested for catalytic activity and stability after a reduction/passivation step. Two catalyst systems have been chosen. These are Pt/Pd/SnO₂ and Pt/Ru/SnO₂.

Under the conditions described above, a characteristic decline in catalytic activity is apparent for both systems, and exit gas temperature has been recognised as a sensitive parameter by which to monitor the activity changes. A semilogarithmic plot of exit temperature as a function of time has revealed two distinct processes connected with the decline in activity: one process is associated with reduction of the oxidised precious metal (at Site A), whilst the other is related to the formation and approach to steady-state of an active site at the metal/support interface (Site B).

Surface species have been identified using on-line Fourier Transform Infrared (FTIR) spectroscopy. Two characteristic absorption bands have been detected. In the case of Pt/Ru, a distinct band at ca. 2055 cm⁻¹ has been identified as linearly adsorbed CO, and a broad, rather weak absorption band at ca. 1890 cm⁻¹ identified as bridge-bonded CO; for Pt/Pd, the corresponding absorption bands are found at ca. 2070 cm⁻¹ and 1870-1890 cm⁻¹ respectively. No marked changes in band intensity could be discerned over a three-hour period under reaction conditions.

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In contrast, flushing with laser gas mix resulted in significant band shifts as well as an attenuation of the bands, consistent with a lowering of the surface coverage of CO. These effects were more pronounced for Pt/Pd. Moreover, in the presence of oxygen alone, the linearly bound species could be removed from the surface in each case. The FTIR studies indicate that high surface coverages of CO are present on the reduced metal under reaction conditions and that upon exposure to air, the reactive CO species is linearly bonded to the precious metal surface. Related CO/O₂ titration experiments on the Pt/Pd monolith have shown that neither reactant displaces the other from the surface and that both spillover and metal/support effects could be associated with these catalysts.

Finally, various poisons and promoters have been added to the catalysts either during preparation or under reaction conditions. In the case of the Pt/Pd system, potassium and manganese act as catalyst poisons at the 1% w/w level. Conversely, in the presence of water (with a relative humidity of ca. 33% at room temperature), manganese stabilises the catalyst. For the Pt/Ru system, the addition of acetone to the feed results in irreversible deactivation. Microreactor pulse experiments have shown that this acetone chemisorbs on the support and indicate that the poisoning effect of acetone is metal/support related. Conversely, water has been shown to be a promoter and stabiliser under present conditions.

A reaction mechanism consistent with the experimental observations has been proposed. It is suggested that under reaction conditions, CO reacts with a surface oxygen atom at Site A, as well as reacting with the support to induce a strong metal/support interaction (Site B). Dissociated oxygen is transported to the precious metal surface via Site B, and water promotes this process. Poisoning is accounted for by adsorption of the rate-inhibiting species at the metal/support interface.

INTRODUCTION

The recombination of CO and O₂, formed during the operation of a sealed E-beam CO₂ laser system, is essential in maintaining the lifetime and integrity of the laser itself. The deployment of heterogeneous catalysts, based on precious metal supported on tin oxide, has been recognised as an important approach with which this problem may be overcome (1). Factors governing the suitability of the heterogeneous catalytic approach are ones of intrinsic

activity, stability (i.e. catalyst lifetime) and tolerance to poisoning under realistic working conditions. These factors have all been addressed in the present study.

EXPERIMENTAL

Materials

Certified gas bottles containing He:N₂:CO₂ in the ratio of 3:2:1 (henceforth termed laser gas mix) and substoichiometric (ca. 2.5:1) CO/O₂ mixtures in laser gas mix (termed reaction gas) were supplied by Air Products Ltd. or Electrochem Ltd. No impurities could be detected by FTIR spectroscopy, and gases were used without further purification. Pure laser gas mix was used to dilute the premixed CO/O₂ in laser gas mix to the required level (typically ca. 5 micromoles O₂/s). Certified bottles containing 1% CO in N₂ and 1% O₂ in N₂ supplied by Air Products Ltd. and cylinders of "white spot" nitrogen (99.99%) and hydrogen (99.998%) supplied by BOC Ltd. were used without further purification.

Ceramic monoliths used in these experiments were manufactured by Corning and had a cell density of 400 per sq. inch. The artifacts were cylindrical in shape with a diameter of ca. 21mm and either 75 mm (Pt/Ru, Pt/Pd/K) or 50 mm (Pt/Pd, Pt/Pd/Mn) in length.

Monolith Preparation and Pretreatment Procedure

Monoliths were coated with metastannic acid and calcined before addition of the active components. These were introduced using standard impregnation techniques. All coated monoliths were then dried and calcined prior to catalyst pretreatment.

The pretreatment routine typically involved an in-situ reduction at ca. 60°C, bringing the hydrogen slowly to 100% using laser gas mix as diluent whilst monitoring the exotherm via a thermocouple situated a few millimetres from the exit of the monolith. Then the system was flushed with laser gas mix and a similar procedure was employed using air instead of hydrogen. This procedure has been termed reduction/passivation.

Test Equipment and Procedures

The test apparatus was a microreactor flow system constructed from 6 mm o.d. stainless steel tubing. The monolith itself was sealed in a glass reactor which was contained within a temperature-controlled incubator. Exit temperatures were monitored by thermocouple, as mentioned above. CO and O₂ levels were detected separately.

The microreactor pulse system consisted of a small section of 6 mm o.d. stainless steel tubing connected to a Perkin-Elmer F11 gas chromatograph with FID detector. 0.5 g samples of catalyst or support (30-80 mesh) were positioned inside the microreactor, and microlitre quantities of acetone were pulsed into the N₂ carrier and over the catalyst bed. The system was calibrated by pulsing acetone through an empty reactor.

FTIR experiments were carried out using a Nicolet 5-DXC Fourier transform infrared spectrometer at 4cm⁻¹ resolution utilising a liquid nitrogen cooled MCT detector. The spectrometer was operated in diffuse reflectance (DRIFTS) mode, using a controlled environment sample chamber (supplied by Spectra-Tech Inc.). The chamber allowed collection of diffuse reflectance spectra of catalysts and infrared active surface species under in-situ reaction conditions. A stainless steel gas flow system was constructed in order to flow laser gas mix and reaction gas through the reaction chamber. The gases were admitted via Brooks Model 5850 TR mass flow controllers, and reaction rates monitored using a Systech EC90M oxygen analyser connected to the gas exit. This system also allowed in-situ pretreatment of the catalyst sample (see figure 1). Samples of powdered Pt/Ru and Pt/Pd monolith were examined, and a typical sample size of 100 mg was used. All catalysts were reduced and passivated in the manner described above and at the appropriate temperature of reaction.

RESULTS AND DISCUSSION

Deactivation Studies

Figure 2 shows the deactivation curve for a Pt/Ru monolith tested under substoichiometric conditions at 4m/s, ca. 60°C, with an oxygen feed rate of 7.9 micromoles/s. After 30 minutes, the reactant feed was stopped, and the catalyst flushed with laser gas mix for one hour. It can be seen from the figure that upon reintroduction of the reactants, the catalyst has regenerated,

indicative of a reversible deactivation process. The exit temperature was monitored and found to closely follow the deactivation trend. A two-step graph was generated on plotting natural logarithm of exit temperature (in Kelvin) versus time (see figure 3). The sensitivity of the temperature parameter can be appreciated from an estimation of the relative error on the points on this graph ($\pm 0.05\%$).

It was also discovered that the Pt/Ru monolith could be fully regenerated by following the reduction/passivation pretreatment described above, and upon readmission of the reactants under similar conditions, an identical deactivation curve was generated. Further, the deactivation trend was reversed over a 30 minute period on effecting a small temperature increase (ca. 8°C). These observations suggest that the decline in activity is related to changes in surface concentrations of reactive intermediates.

The exit temperature plots for the Pt/Pd and Pt/Pd/Mn monoliths (tested under the same conditions as the Pt/Ru monolith) are shown in figure 4. Again the two regimes can be easily distinguished.

On comparing the CO and O₂ deactivation traces for these catalysts, it was noted that over the initial minutes of reaction, the CO concentration fell sharply below the O₂ concentration, indicative of a surface reduction process. After several minutes the two traces yielded the corresponding deactivation rates expected for stoichiometric reaction.

The activity changes characteristic of Pt/Pd and Pt/Pd/Mn under dry-gas conditions were not repeated under wet-gas conditions. The same monolith samples were tested under identical conditions, except with a relative humidity of ca. 33% at room temperature in this case. The resultant exit temperature plots are shown in figure 5. It is evident that the water has a net promoting and stabilising effect, although of the two catalysts, the manganese-containing one appears to have the better stability.

The effect of potassium on catalyst performance was investigated by testing the activity of the Pt/Pd/K monolith at 4m/s, ca. 60°C , with an oxygen feed rate of 7.9 micromoles/s. With regard to initial activity, gross deactivation was observed relative to the non poisoned Pt/Pd monolith. The characteristic exit temperature plot generated from the exit temperature is shown in figure 6. It should be pointed out here that the rate of deactivation in the second stage (as measured by the gradient on the graph) is very close to that for the non poisoned catalyst. In fact, potassium decreases the initial activity of the catalyst without significantly affecting the Pt/Pd deactivation profile.

That initial decrease could be explained by an increase in the CO self-poisoning effect, based on evidence from the surface science literature where it has been shown that K increases the heat of adsorption of CO on Pt (2). Other evidence reported below would lead to the conclusion that both K and Mn affect the oxidisability of the precious metal, but this could well be via an increase in the strength of CO chemisorption on the metal.

Poisoning Studies

In order to assess the effects of various potential catalyst poisons on the rate of reaction, microlitre quantities of acetone, hexane, water and chloroform were injected into the feed and over the previously reacted Pt/Ru monolith at 2m/s with an oxygen feed rate of 3.8 micromoles/s and a substoichiometric gas ratio. The catalyst had been reduced and passivated at room temperature prior to reaction. The corresponding deactivation curves are shown in figures 7-9 (n.b. the semilogarithmic plot is used merely as a convenient way of representing the data in this case).

Figure 7 shows that the deactivation rate increases with the introduction of acetone into the gas feed. Subsequent injections do not appear to have as significant an effect on the catalytic rate. The deactivation curve for a non poisoned Pt/Ru monolith section, tested under identical conditions and after a similar pretreatment, is shown by the dotted deactivation curve. It may be noted here that although the dotted deactivation curve illustrates the effect of acetone on the initial and overall deactivation, the deactivation rate appears to be greater for the fresh versus reacted monolith section over the initial stages of the reaction.

The same Pt/Ru monolith was given the reduction/passivation pretreatment at room temperature as before and retested under identical reaction conditions. It is evident from figure 8 that the initial activity has dropped by ca. 25% compared with the value observed in figure 7. This correlates well with the net deactivation at steady-state of ca. 20% found in figure 7 and indicates that this deactivation is irreversible under present pretreatment conditions.

In order to further investigate the nature of the poisoning effect of acetone, a parallel series of experiments were performed (with reference to the support) on powdered samples of Pt/Ru/SnO₂ and Pt/Pd/SnO₂ catalysts using the microreactor pulse system. The samples were subjected to the reduction procedure described earlier, except now at room temperature and using nitrogen as diluent instead of laser gas mix. It was found that the quantity of acetone taken up by the support corresponded

to ca. 5 microlitres (ca. 68 micromoles) and that this quantity of acetone was indistinguishable from that taken up by the catalysts. From the BET surface area of the catalyst support (ca. 130 m²/g), it was estimated that this value corresponded to approximately one-fifth of a monolayer of acetone. The temperature was ramped up to 90°C, whereupon neither desorption nor dissociation of acetone could be detected by FID.

These experiments can be used to explain the net deactivation observed over the Pt/Ru monolith sample. They strongly support a deactivation mechanism which involves the blocking of active sites on the support which in turn lower the average rate of reaction on the surface of the catalyst. This would explain why a molecule which would not have been expected to chemisorb strongly on the metal under reaction conditions has a significant effect on the deactivation rate. The results could support a spillover type mechanism, such as that proposed by Bond and co-workers (3), but would also be consistent with a system in which the metal was strongly interacting with the support to produce active sites.

Figure 8 also shows the cumulative effect of pulsed injections of hexane and water on the Pt/Ru monolith. In the case of hexane, the results suggest that this compound is a poison, and the poisoning effect appears to be a function of hexane partial pressure. However, it is also evident that the hexane injection induces stability in the catalyst system. Since it is unlikely that hexane molecules would chemisorb on the support at these reaction temperatures, the effects observed may be a function of an impurity such as hexene. In comparison, water acts as a promoter under present conditions. The figure shows a sharp transient increase in activity, indicative, perhaps, of the removal of a surface poison from the catalyst. This transient increase in activity would seem to be practically independent of pulse size. In addition to this behaviour, water appears to have a net promoting effect on overall activity (~15%).

Finally, figure 9 shows the further effect of added chloroform. Now the net effect is that of a poison, with the activity changes mirror images of those observed for water. It is plausible that chloroform induces poisoning via Cl⁻ transfer to the active metal, as chlorides have been associated with the blocking of active Ru sites which chemisorb CO (4). However, other studies have also indicated that Cl⁻ would weaken the CO bond (5), suggesting that Cl⁻ should decrease the effects of self-poisoning (should they be present here). An alternative model for chloride poisoning will be explored below.

FTIR Experiments

The FTIR work was designed to look at concentrations of surface species at the very early stages of reaction, where it was believed that the most significant changes on the surface would occur. Carbonyl absorption band assignments were primarily based upon those outlined in the review of Sheppard and Nguyen (6), and only the frequency range of significance ($1300 - 2600 \text{ cm}^{-1}$) has been displayed in the figures.

In order to discover the nature of CO chemisorption on these catalysts, the Pt/Ru catalyst was reduced and then CO introduced to the sample in a stream of laser gas mix. An absorption band at 2052 cm^{-1} was present, and this band shifted downward to 2044 cm^{-1} upon stepwise heating in a flow of helium (see figure 10). This band is assigned to a linearly bound carbonyl group. It is evident from the figure that CO is strongly bound to the surface, since the band intensity does not decrease significantly even at 250°C . However, this species evidently reacts (or is displaced) upon exposure to air, since the carbonyl absorption band is completely removed from the spectrum.

The reduction/passivation process was next investigated at the end of each stage. Spectra were taken after the reduction stage using pure hydrogen and then after flushing with laser gas mix, after admission of pure air and after a final flushing with laser gas mix. The spectra are shown in figure 11. No bands could be distinguished after a hydrogen pretreatment. Upon flushing with laser gas mix, a band at ca. 2035 cm^{-1} and a rather weak absorption band at ca. 1890 cm^{-1} were assigned to linear and bridge-bonded carbonyl species. These two bands have frequencies which fall in the ranges expected for low surface coverages of CO associated with bimetallic particles of an alloy such as ruthenium/platinum. The reason for the CO bands must be dissociative chemisorption of CO_2 on the reduced metal. Upon exposure to air, the linearly bound species was removed and a distinct broad band associated with molecularly adsorbed water appeared at ca. 1650 cm^{-1} . This water is assumed to be a by-product of the reduction/oxidation process. Identical behaviour was observed in the case of Pt/Pd, with the corresponding absorption bands appearing at ca. 2030 cm^{-1} and 1870 cm^{-1} . Carbonyl band frequencies such as these are consistent with those reported for low surface coverages of CO on metals such as platinum or palladium where linear and bridge-bonded carbonyl groups are associated with metal sites of low coordination number.

The FTIR spectra recorded for Pt/Ru and Pt/Pd catalyst under reaction conditions are shown in figures 12-17, and the corresponding absorption bands tabulated in Table 1. These

catalysts were examined at high flow rates (1 l/min) with no detectable conversion, and lower flow rates (100 ml/min) with ca. 20% conversion and no deactivation over a 2-3 hour period. With regard to the spectra, it should first be noted that the small rises observed at ca. 2170 cm^{-1} and 2120 cm^{-1} are due to gas phase CO. In summary, two distinct absorption bands at ca. 2055 cm^{-1} and 1890 cm^{-1} were detected for Pt/Ru (see figures 12-14); the corresponding absorption bands for Pt/Pd were detected at ca. 2070 cm^{-1} and $1870/1890\text{ cm}^{-1}$ (see figures 15 and 17). These bands are consistent with those reported for saturated surface coverages of linear and bridge-bonded carbonyl species on supported Ru/Pt and Pd/Pt catalysts in the reduced state. In all cases the bands were of similar intensity throughout the period of reaction, even when the reaction rate was observed to increase significantly (~50% for low flow experiments). It is apparent, then, that these intermediates quickly attain a steady-state concentration on the surface, and their reactivity cannot therefore be assessed from these experiments. Nonetheless, it should be noted that in the case of Pt/Pd, flushing with laser gas mix reduces the intensity of the linearly bound absorption band as does exposure to air (see figure 16). Flushing with laser gas mix does not appear to have as significant an effect in the case of Pt/Ru (cf. top spectra from figures 12-14).

A final piece of information relates to the FTIR spectra for the Pt/Pd sample tested at low flow rate (figure 17). The asymmetry of the linearly bound carbonyl band was more pronounced here, and a shoulder could be distinguished at ca. 2100 cm^{-1} because of lack of interference from bands due to gas phase carbon monoxide. The position and appearance of this shoulder is indicative of CO bound linearly to partially oxidised metal particles of platinum/palladium. From these observations it has been concluded that the platinum/palladium component is heterogeneous in nature.

CO/O₂ Titration Experiments

To assess the oxidation/reduction behaviour of these catalysts, the regenerated Pt/Pd monolith was reduced in H₂ or CO and then oxidised at ca. 62°C (using nitrogen as a diluent) and the CO/O₂ uptakes measured using the flow system described earlier.

It was immediately noted that neither CO nor O₂ displaced each other from the surface. Further, the O₂ uptake corresponded to ca. 30 ml, independent of reducing agent used.

In contrast, the amount of CO used to reduce the monolith was ca. 58 ml; in other words, within experimental error, the reaction of CO with O₂ on the surface was found to be stoichiometric. Significantly, if the catalyst had been completely oxidised beforehand, as is suggested above, this CO must have reacted (at least in part) directly from the gas phase. Further, assuming approximately 1:1 metal to CO stoichiometry, these results would suggest that after a CO reduction, the net CO uptake on the metal would be ca. 30 ml.

Next, the oxidised monolith catalyst was reduced with H₂ and the CO uptake recorded at ca. 62°C. The amount of CO adsorbed on the catalyst was ca. 12 ml. This value is much lower than that expected on the basis of corresponding CO and O₂ uptakes and indicates either that the reduced metal is strongly interacting with the support (thus suppressing CO chemisorption), or perhaps O₂/CO spillover, or indeed a combination of these effects.

This last experiment was repeated using wet gas (saturated water vapour at room temperature) with ca. 100 ppm O₂ impurity in the gas feed. An identical CO uptake was recorded, indicating that water does not significantly suppress this behaviour.

Finally, in order to relate this data to the reaction itself, the uptake of CO was determined during the initial stages of reaction from an integration of the CO and O₂ analyser traces for the Pt/Pd monolith (as reported above). After 6 minutes, the CO and O₂ uptakes were 94 ml and 36 ml respectively (i.e. a net CO uptake of ca. 22 ml); the values over a further 4 minutes were found to be 46 ml and 23 ml respectively (i.e. stoichiometric reaction). Thus, it would appear that the surface of the catalyst is up to 38% "reduced" under substoichiometric conditions (n.b. the relative amounts of reacted and adsorbed CO cannot be determined here). The corollary to this conclusion is that the catalyst is not less than 62% "oxidised". If this oxygen was solely associated with the metal (i.e. surface oxygen atoms), the reaction would be predicted to be close to zero-order in oxygen. However, this is not consistent with the literature, where it has been reported (under similar conditions) that the reaction is zero-order in CO and first-order in O₂ (1). Thus, it is more likely that most of the oxygen is associated with the support, possibly in an associatively bound state at the metal/support interface.

If this model is correct, then the passivation step introduces oxygen into the support, and this oxygen can be removed by reaction with CO or H₂, probably via a spillover mechanism. Such a model is supported by isotopic labelling studies (7).

Proposed Reaction Mechanism

Any reaction mechanism which explains the experimental results has to account for the abrupt change highlighted by the exit temperature (after ca. 20 minutes) and also the poisoning phenomenon encountered with added gas components.

It is suggested that the overall decline in activity is accounted for by two distinct catalytic sites and that one of these (Site A) is associated solely with the precious metal (PM) (refer to figure 18). Upon a reduction/passivation pretreatment, carbon monoxide reacts from the gas phase with a reservoir of surface oxygen to form carbon dioxide at site A (STEP 1). CO quickly attains a saturation level on the reduced part of the metal surface (as suggested by FTIR) and probably reacts in the linearly bound form with oxygen at an adjacent Site A. (STEP 1 (a)). Further, gas phase CO continually reacts with the support to induce a precious metal (PM)/Sn interaction (Site B) (STEP 2). This site is produced under net reducing conditions and does not chemisorb CO readily. Site B reacts by dissociating O_2 across the PM/Sn interface to produce Site A plus non interacting SnO_2 (STEPS 3-4). The slow decline in activity is regarded as simply an approach to steady-state (STEP 5).

In summary, catalytic reaction is proposed to involve gas phase and linearly adsorbed CO molecules which can reduce the metal oxide (Site A) to metal as well as reducing the support (probably via spillover). This latter reduction induces a metal/support interaction, producing a second catalytic site (Site B) that can dissociate O_2 to regenerate Site A. On doing so the metal/support interaction (i.e. Site B) is destroyed. The overall process is therefore oscillatory.

This mechanism accounts for the stepped change mentioned above, with Site A depleting rapidly as Site B builds up in concentration. Site B reaches a maximum concentration and then decays to a steady-state concentration. The activity pattern outlined in figure 6 could be evidence for the buildup and decline in concentration of Site B if water was maintaining the concentration of Site A. Here the rate-determining step would shift from being that of oxygen transfer to the metal (via Site B) to that of CO oxidation at the surface itself. From a comparison of the initial exit temperatures shown in figures 5 and the corresponding steady-state exit temperatures shown in figure 6, it is evident that the water-promoted catalysts do indeed approach the initial exit temperatures found in the corresponding dry-gas reaction. These observations are consequently in line with the above suggestion.

The promotional effect of water can therefore be explained in terms of an increase in the rate of transfer of dissociated oxygen to the precious metal. The sharp increase in activity shown in figure 9 is caused by a transient increase in the concentration of Site A, and the net stabilising effect of water is accounted for by a change in the rate-determining step of the reaction.

Poisoning is accounted for by chemisorption of molecules at Site B. Compounds that can form a stable transition state are potential poisons which either block Site B or produce an inactive Site A (e.g. Cl^- transfer in the case of chloroform). Acetone and chloroform are particularly suitable for bonding to Site B via the oxygen and chloride atoms respectively.

The regeneration of the monolith upon heating or flushing with laser gas mix can be regarded as a reoxidation of the metal, with Site A being formed from Site B via a kinetically slow step. This process has also been reported elsewhere (8).

There is strong experimental evidence for PtSn alloying in the literature. Temperature programmed reduction studies on alumina-supported Pt/Sn systems have shown that PtSn alloys are indeed feasible in the presence of hydrogen, albeit at elevated temperatures (9). More recently the NASA group, utilising ion-scattering spectroscopy, have reported PtSn alloy formation upon CO reduction (10). Unfortunately, the FTIR spectra produced in this study cannot be used to directly determine the existence of a metal/support interaction, since even the alloying effect produces a negligible shift in the absorption frequency of CO on the precious metal (11).

An alternative mechanism for CO oxidation over Pt/SnO₂ has been recently proposed (12). Reaction and deactivation are proposed to occur via the formation of surface hydroxyl and carbonate/bicarbonate species. No evidence has been found in the FTIR spectra to indicate that these intermediates exist under the experimental conditions used in this study. If such species were present, absorption bands would be expected at ca. 3600 cm^{-1} , 1530 cm^{-1} and 1390 cm^{-1} respectively.

It should be concluded here that reaction on these catalysts is complex and that further study is needed to understand the elementary steps involved in the CO oxidation process. Of particular relevance would be kinetic and isotopic work.

GENERAL CONCLUSIONS

From the present work a number of general conclusions may be made regarding the CO oxidation reaction under possible laser operating conditions:

1. For Pt/Ru and Pt/Pd systems supported on tin oxide and prepared in the manner described above, an inherent two-stage reaction process is observed, the extent of which can be conveniently monitored by a change in the reaction exotherm.
2. The initial process is believed to be a decrease in the level of oxidised metal, which can be partially recovered by heating or by flowing inert laser gas mix over the catalyst.
3. Potassium and manganese act as poisons when added to the Pt/Pd catalyst at the 1% w/w level. Both are thought to be associated with lowering of the oxidisability of the precious metals.
4. Addition of acetone to the gas feed has been shown to be detrimental to the activity of a Pt/Ru catalyst, resulting in irreversible deactivation. This is believed to be due to irreversible chemisorption of acetone on the support, and suggests a probable metal/support interaction, the extent of which is a function of chemisorption on the support. Water, on the other hand, has been shown to enhance the activity as well as stability of these catalysts. This is thought to be due to water promoting the rate of oxidation of the metal via the metal/support interface.
5. FTIR results have shown that under reaction conditions two modes of CO chemisorption co-exist on the reduced precious metal surface: these are linearly bonded and bridge-bonded CO. A high surface coverage of CO is probable, and in the presence of oxygen alone, the reactive species is not bridge-bonded but linearly bonded CO. However, under reaction conditions these species quickly attain a steady-state concentration, and their surface concentrations do not change significantly with time even when the reaction rate is changing considerably.
6. The cumulative evidence supports a reaction scheme in which two, interdependent, active sites are involved in CO oxidation under pseudo-operating conditions. One site is mainly associated with the metal function of the catalyst whilst the other is intrinsically dependent upon the metal/support interface.

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**TABLE I. ABSORPTION BAND POSITIONS AND ASSIGNMENTS
FOR CATALYSTS UNDER REACTION CONDITIONS**

FIG.NO.	CONDITIONS	M-CO (cm^{-1})	M ₂ -CO (cm^{-1})	H ₂ O SURFACE (cm^{-1})
10	CO ADS. IN LM AT RT REDUCED IN H ₂ ONLY	2052	-----	-----
12	REACTION AT RT 1 l/min RX (PRETREAT. AT RT)	2059	c.1890(w)	-----
	1 l/min LM	2052*	c.1890(w)	-----
13	REACTION AT 50°C 1 l/min RX (PRETREAT AT 50°C)	2059	c.1890(w)	-----
	1 l/min LM	2049 [.]	c.1890(w)	-----
14	REACTION AT RT 0.1 l/min RX (PRETREAT. AT RT)	2054	-----	-----
	1 l/min LM	2054 [.]	-----	-----
15	REACTION AT RT 1 l/min RX (PRETREAT AT RT)	2072	c.1870	c.1640
	1 l/min LM	2049 ^{**} (sh.2100)	c.1850	c.1640
17	REACTION AT RT 0.1 l/min RX (PRETREAT. AT RT)	2071 (sh.)	c.1890	c.1640
	1 l/min LM	2047 ^{**}	c.1850	c.1640

GLOSSARY

- * Slight attenuation of band on exposure to laser mix
- ** Attenuation of band on exposure to laser mix
- w Weak in intensity
- sh. Shoulder
- RX Reaction mixture
- LM Laser mixture
- cm⁻¹ Wavenumber
- RT Room temperature

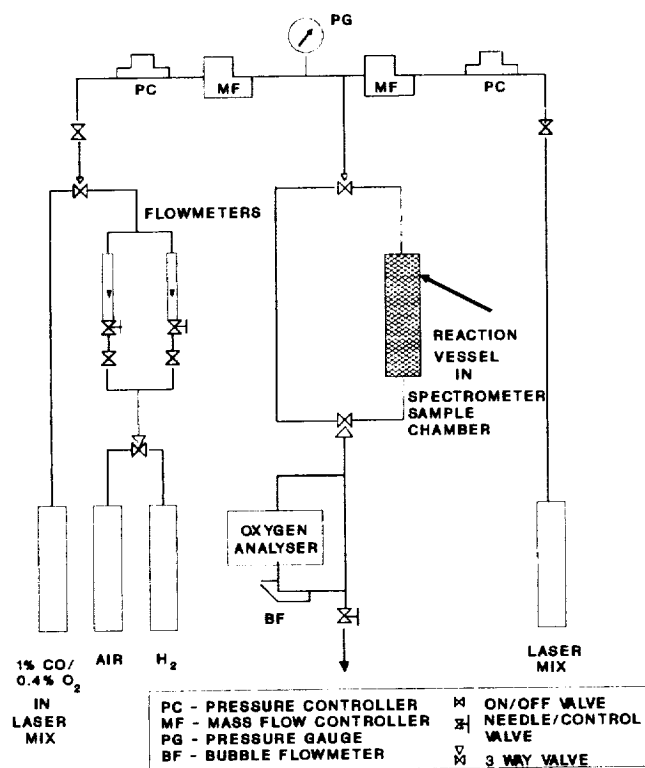


Fig.1 - FTIR REACTION SYSTEM

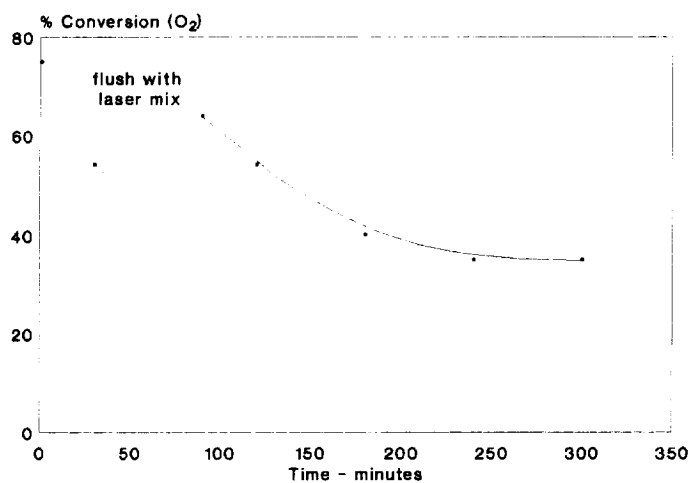


Fig.2 - Deactivation curve for Pt/Ru monolith at 4m/s

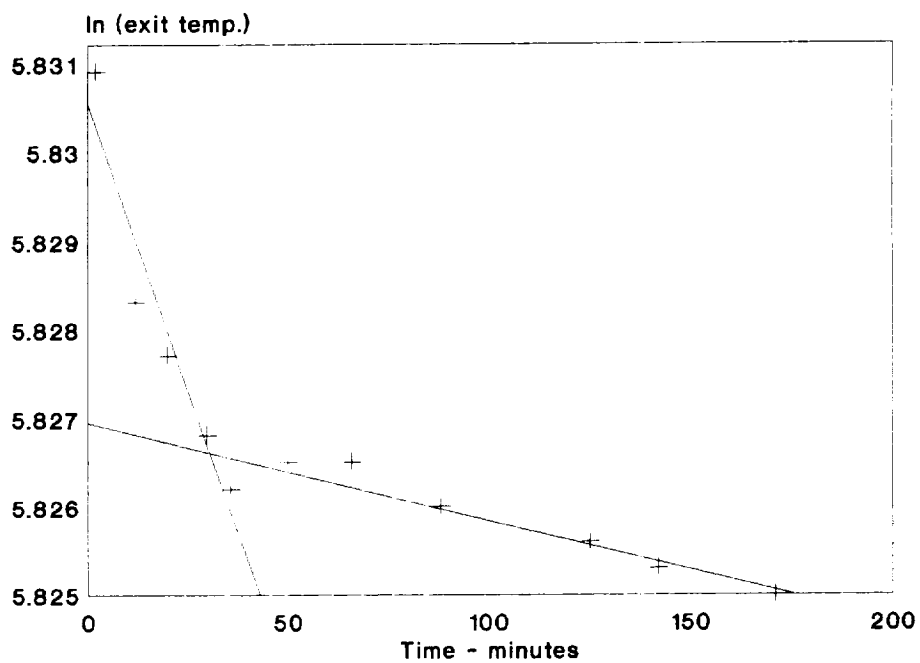


Fig.3 - Pt/Ru Monolith tested at 4 m/s

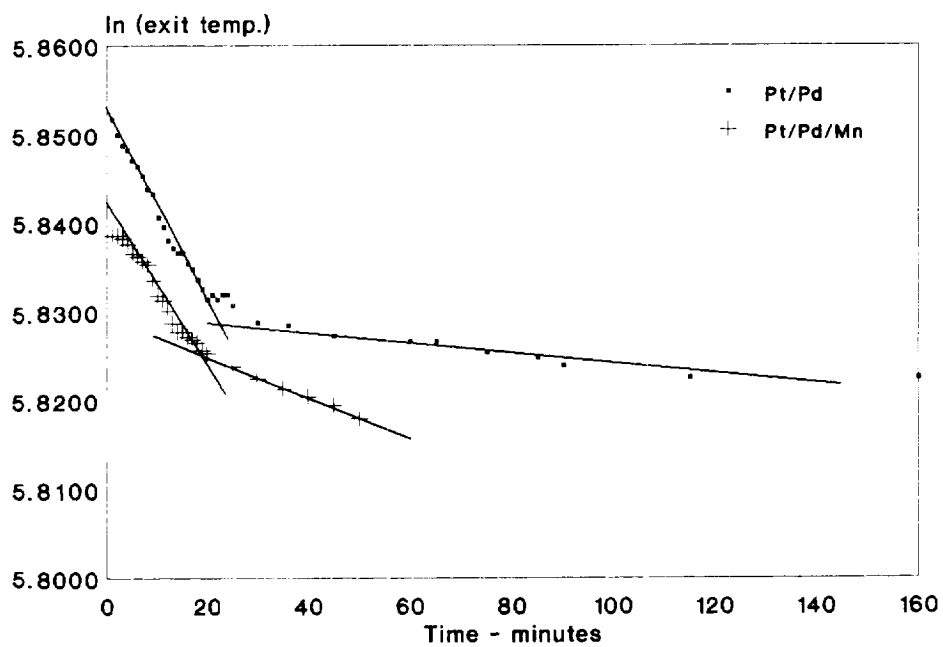
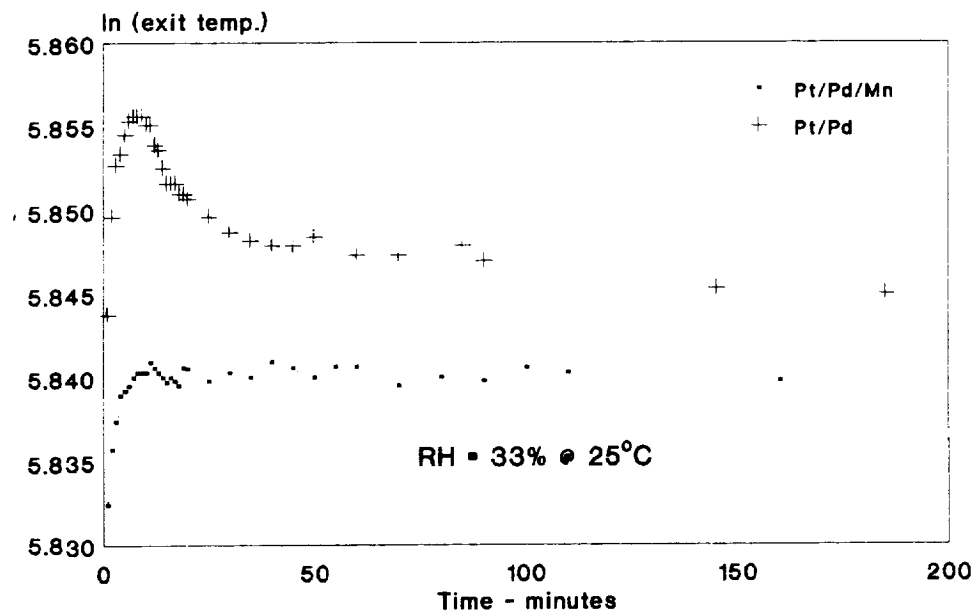


Fig.4 - Pt/Pd Monoliths tested at 4 m/s



**Fig.5 - Pt/Pd monoliths tested at 4 m/s
in the presence of water**

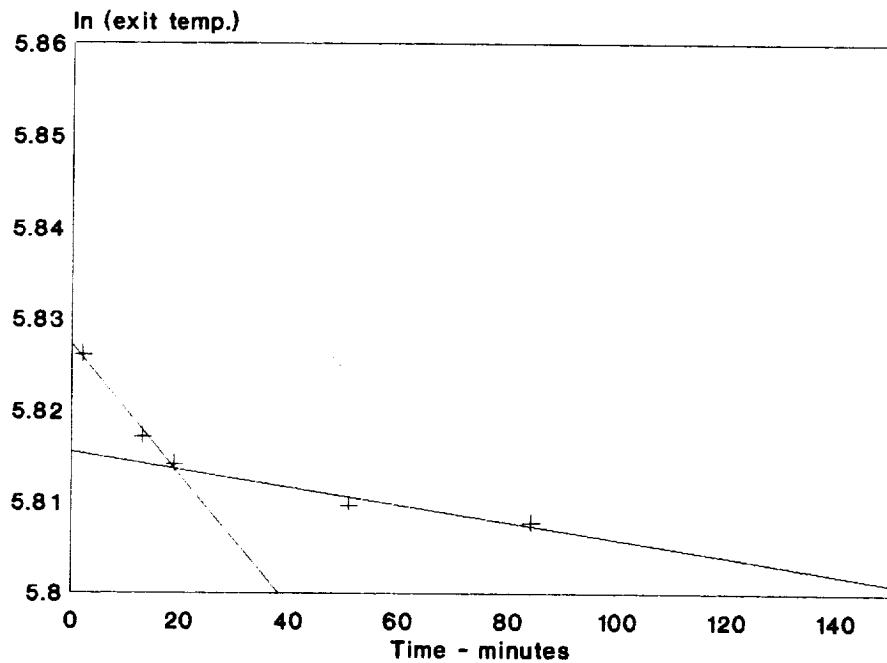


Fig.6 - Pt/Pd/K Monolith tested at 4 m/s

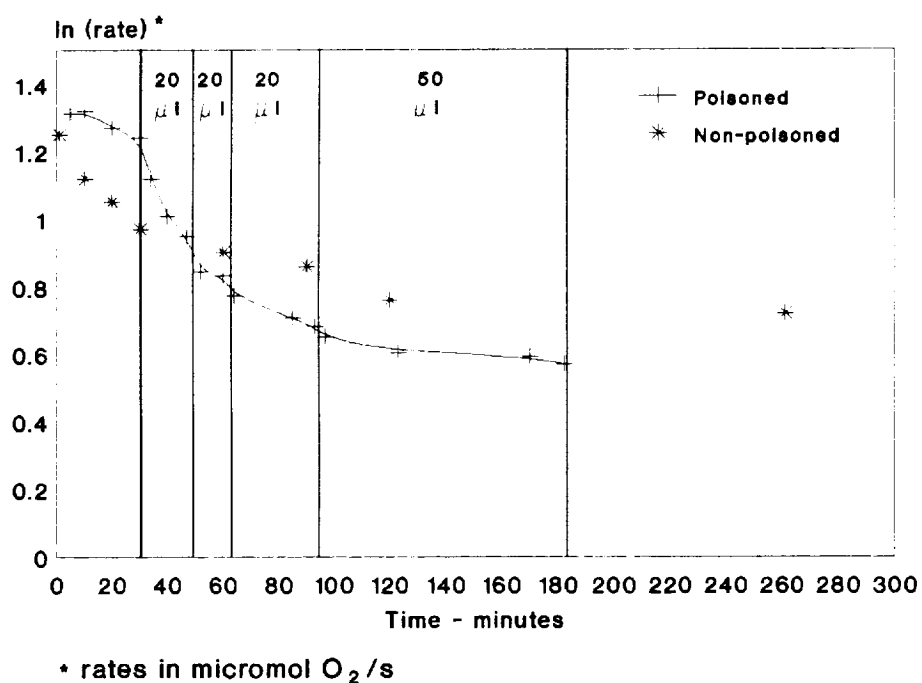


Fig.7 - Deactivation profile for a fresh vs. regenerated Pt/Ru monolith with added acetone

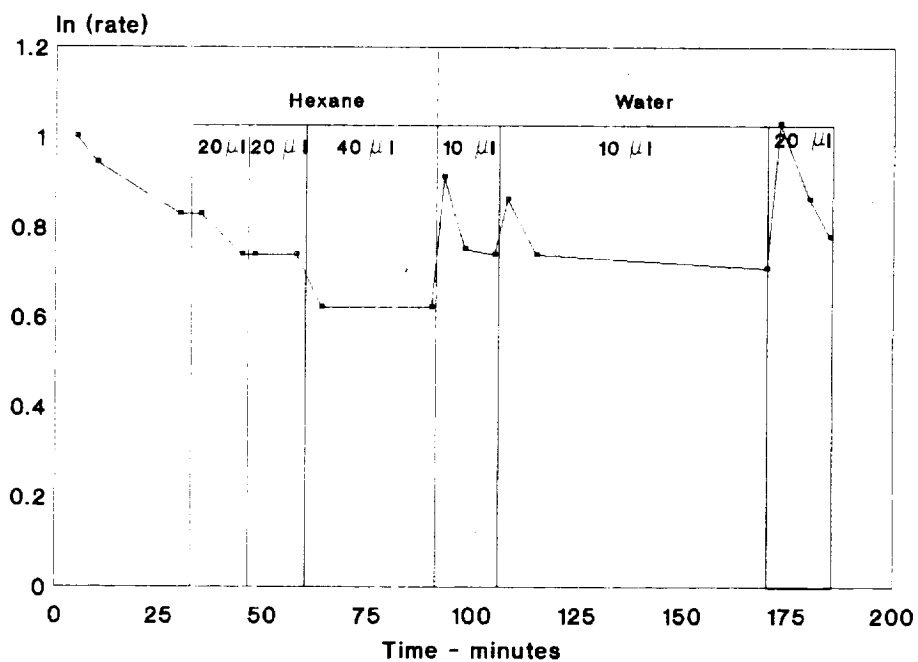


Fig.8 - Cumulative deactivation profile for a deactivated Pt/Ru monolith with added hexane and water

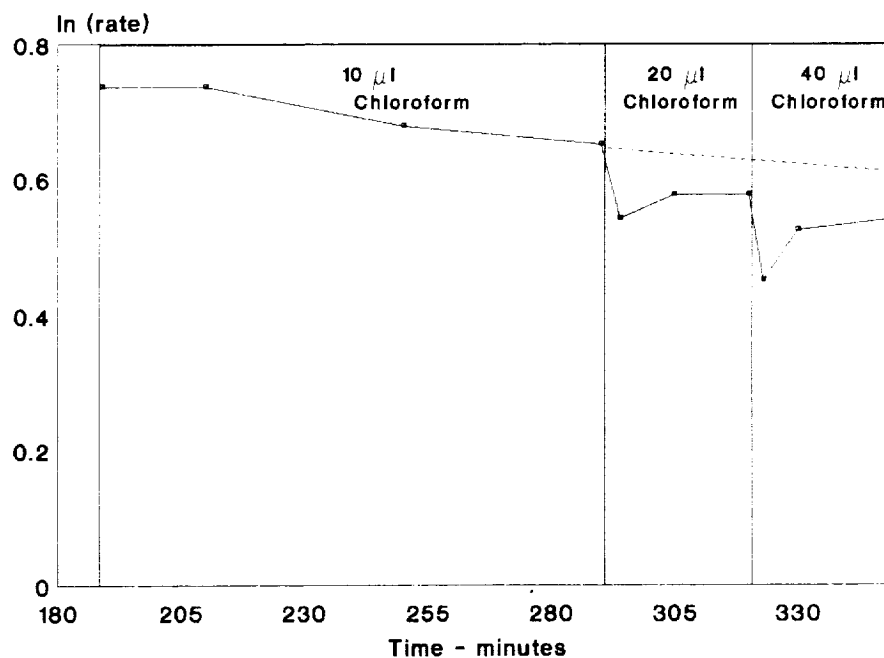


Fig.9 - Cumulative deactivation profile for a deactivated Pt/Ru monolith with added hexane, water and chloroform

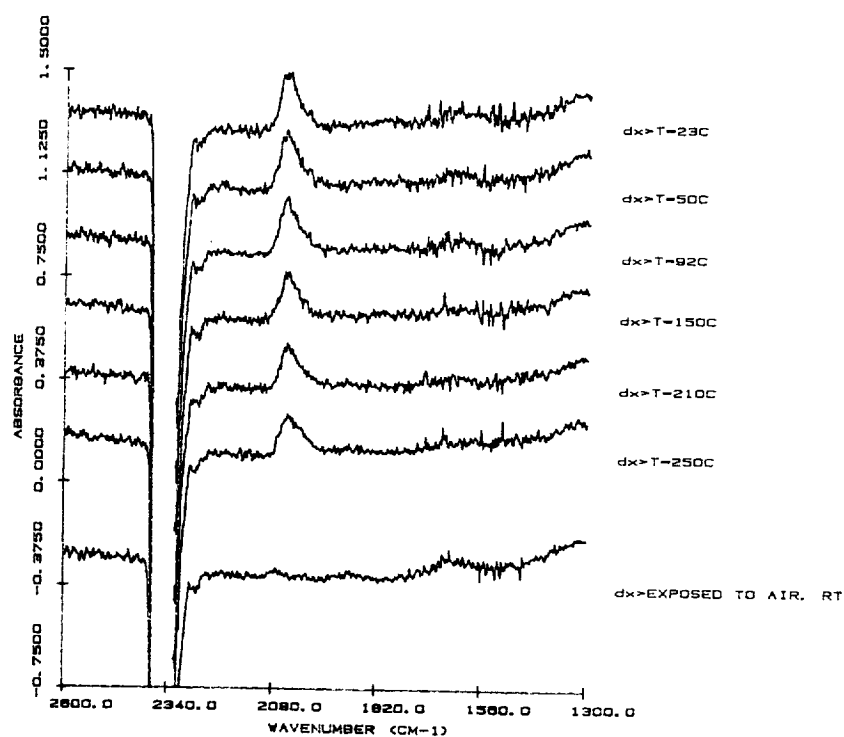


Fig.10 - FTIR Spectra showing CO desorption/reaction on Pt/Ru in Helium/Air

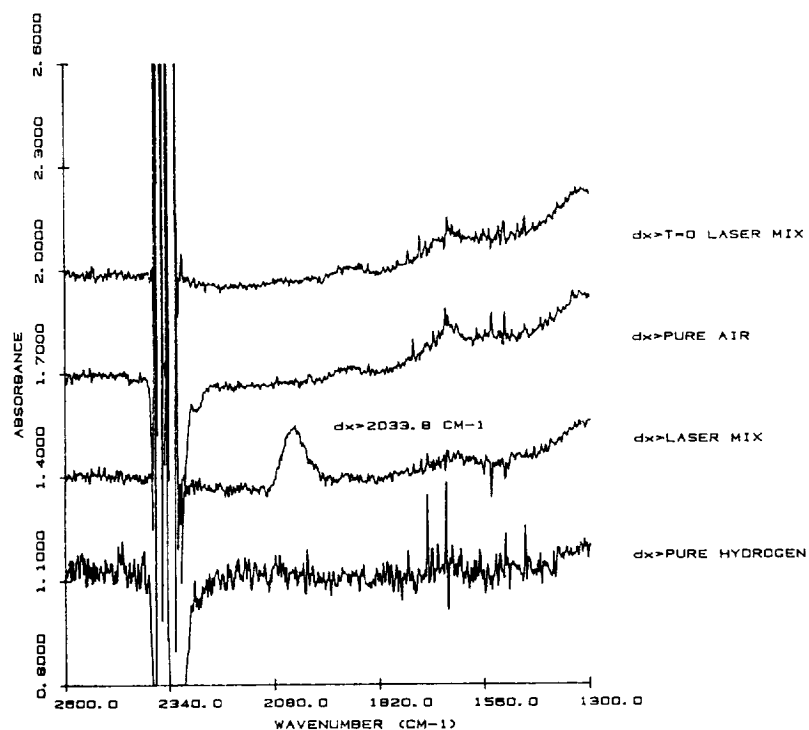


Fig.11 - FTIR Spectra showing CO₂ dissociation/CO reaction on Pt/Ru during pretreatment

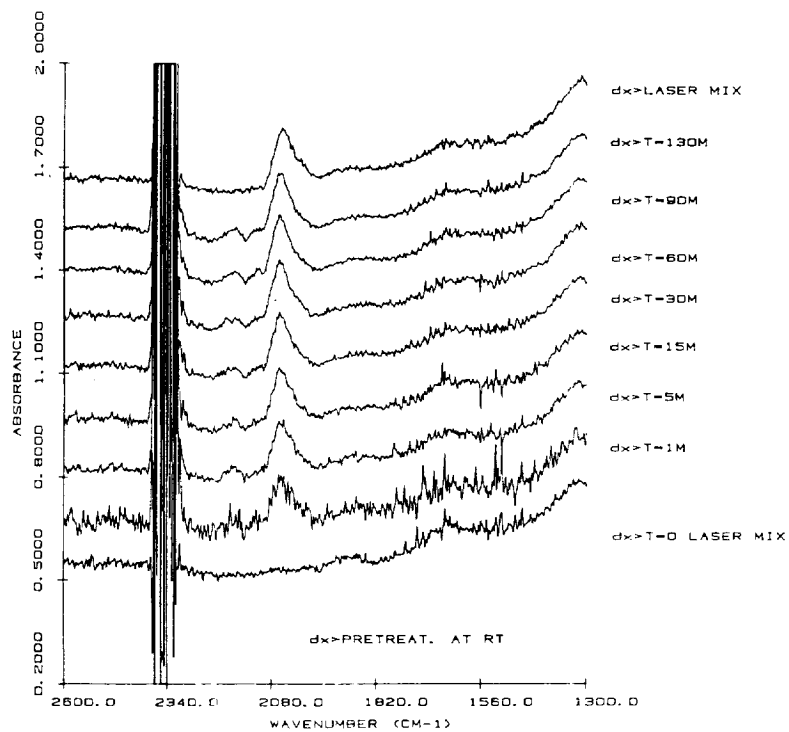
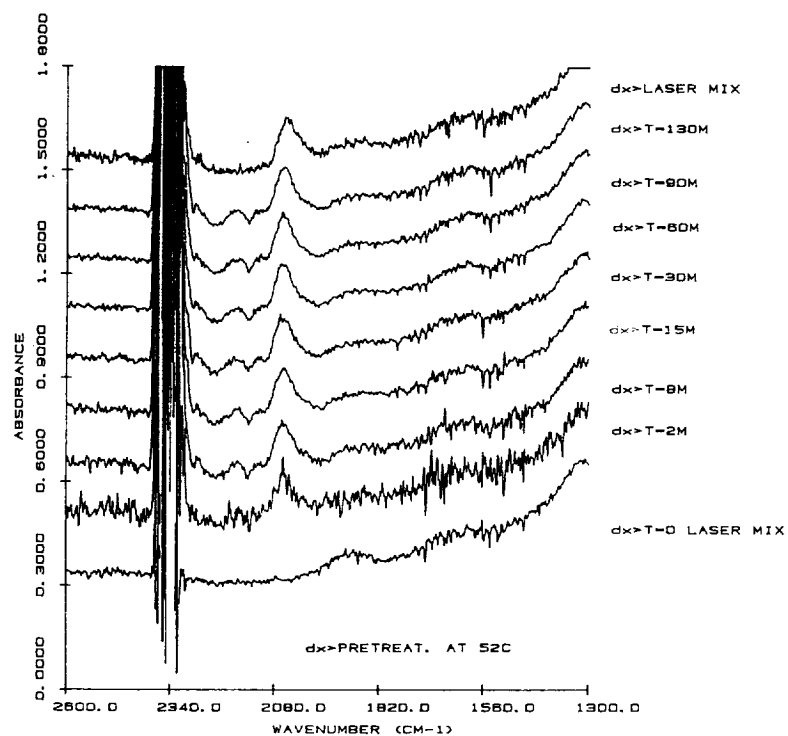
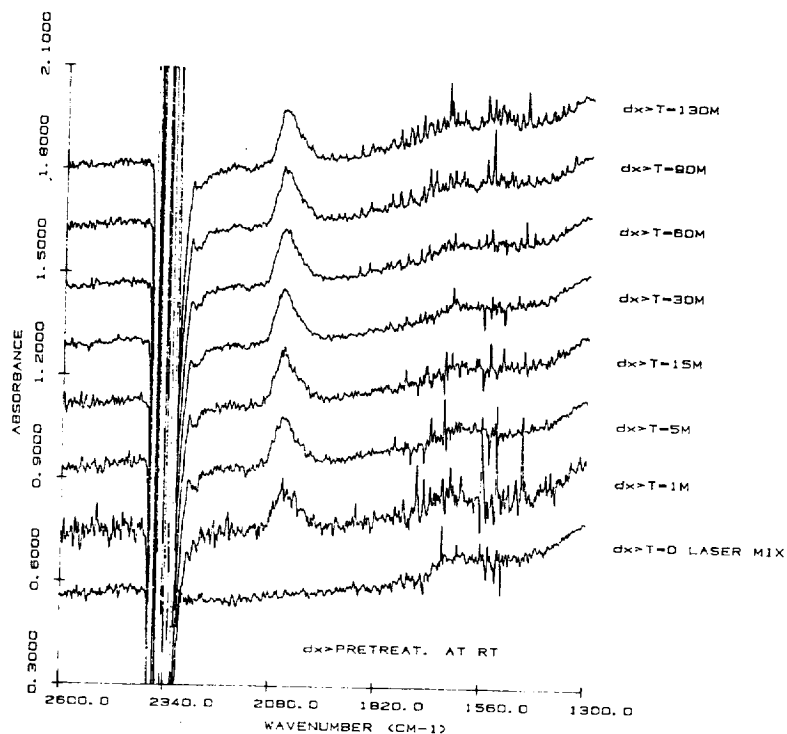


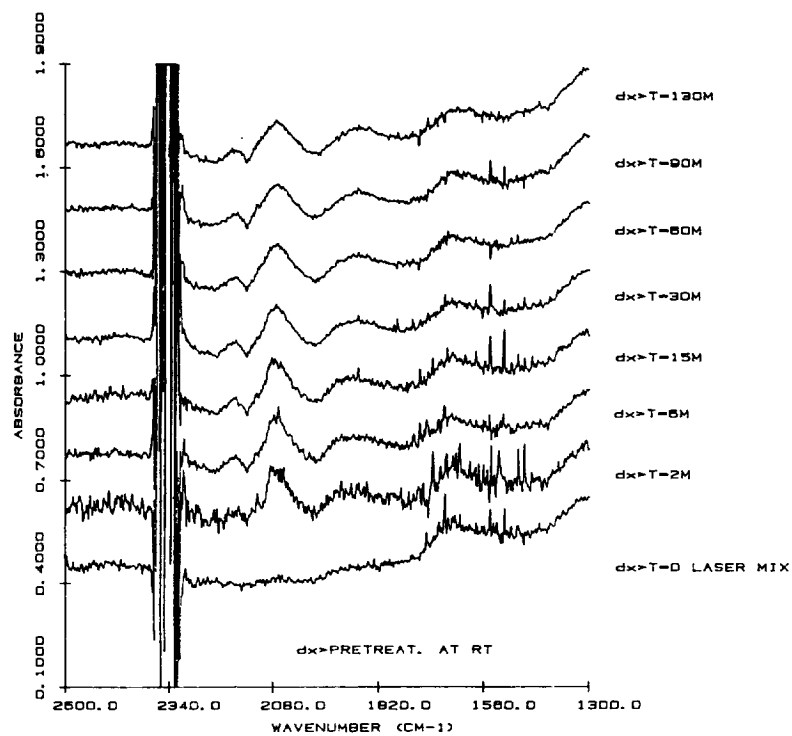
Fig.12 - FTIR Spectra for Pt/Ru with 1 l/min reaction gas at room temperature



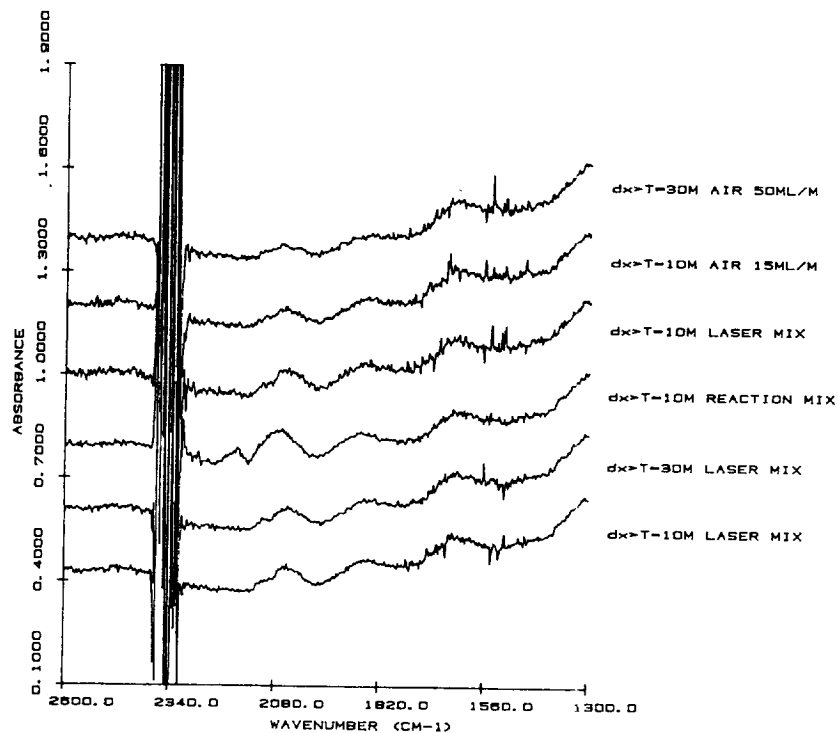
**Fig.13 - FTIR Spectra for Pt/Ru with 1 l/min
reaction gas at 52°C**



**Fig.14 - FTIR Spectra for Pt/Ru with 100 ml/min
reaction gas at room temperature**



**Fig.15 - FTIR Spectra for Pt/Pd with 1 l/min
reaction gas at room temperature**



**Fig.16 - FTIR Spectra for reacted Pt/Pd
on flushing with laser mix and air**

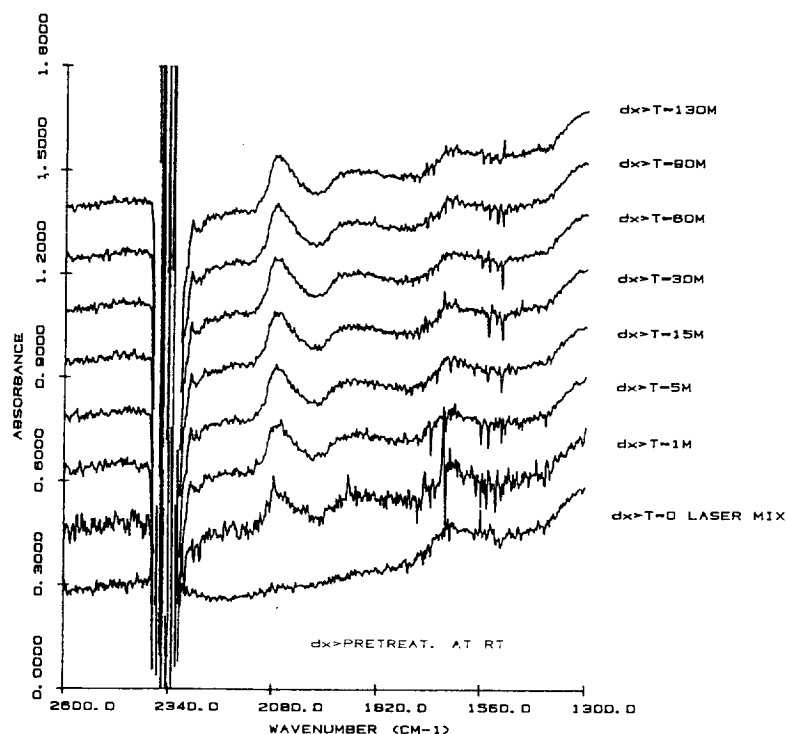


Fig.17 - FTIR Spectra for Pt/Pd with 100 ml/min reaction gas at room temperature

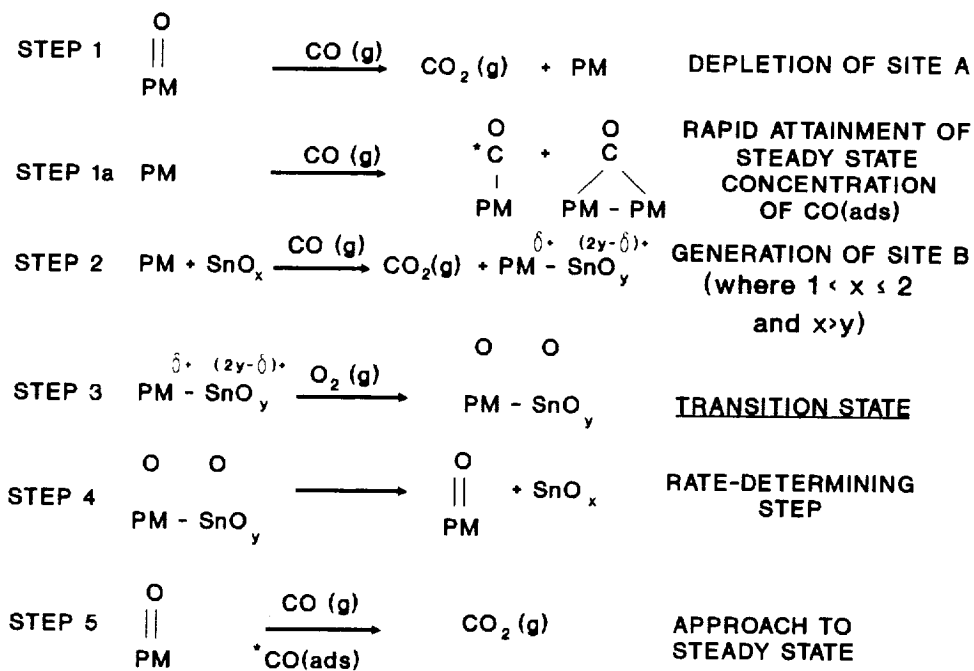


FIG.18 - PROPOSED REACTION MECHANISM FOR LASER CATALYSTS